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(71) Applicant: SOCIETE DES PRODUITS NESTLE S.A.
Case postale 353
CH-1800 Vevey(CH)

(72) Inventor: Burros, Byron
12201 Stewarton Drive
Northridge, Ca. 91325(US)
Inventor: Einerson, Mark A.
25632 Serena Drive
Valencia, Ca. 91355(US)
Inventor: Tran, Kha
2445 N. Burlingham Place
Simi Valley, Ca. 93063(US)

(54) Dried fat emulsion product and method of producing the same.

(57) Dried fat emulsion products having improved resistance to oxidation at elevated temperatures are produced by the two stage encapsulation of oil or fat globules with a hydrophilic film forming material. An aqueous dispersion of an edible fat or oil, a hydrophilic film forming material, a carbohydrate and water is emulsified to form an oil-in-water emulsion concentrate in which fat globules are encapsulated by the film forming material. After formation of the emulsion concentrate, a second portion of a hydrophilic film forming material is added to the emulsion concentrate in an amount substantially equivalent to the amount of film former in the aqueous dispersion, to provide an additional coating layer of film forming material encapsulating the fat globules. This second portion of film forming material may be added to the emulsion prior to or subsequent to drying of the emulsion concentrate.

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DRIED FAT EMULSION PRODUCT AND METHOD OF PRODUCING THE SAME

This invention relates to an improved dried fat emulsion product and to the method of producing the improved emulsion product. More particularly, the invention relates to the production of edible dried fat emulsions having improved resistance to oxidation, particularly at elevated temperatures.

Dried fat emulsions have found wide acceptance in numerous convenience food products such as cake mixes, powdered shortenings, dried coffee whiteners, flavorings, topping mixes, sauce mixes, dried beverage mixes, and the like. Typically such dried emulsions are prepared by emulsifying fat or oil in an aqueous dispersion or solution of an edible hydrophilic film forming material, such as proteinaceous materials, hydrocolloid gums, starches, carboxymethylcellulose, and the like, to form an oil-in-water emulsion concentrate which is then dried, such as by spray drying. In the dried emulsion, fat globules are encapsulated by a layer of the film forming material. Such dried fat emulsions provide the advantages of ease of handling and incorporation with other dry ingredients in the preparation of various food products. Moreover, since fats are susceptible to oxidative deterioration in the presence of air, causing development of rancid odor and taste, encapsulation of the fat globules by the film forming material retards rancidity development of the fat and thereby provides the fat containing product with a longer shelf life.

Frequently there is a need for dried fat emulsion products having greater resistance to oxidation, and hence a longer shelf life, than can be obtained by the procedure described above. However, prior procedures intended to produce dried fat emulsions having increased resistance to oxidative deterioration have not been entirely satisfactory. For example, one approach to inhibit the development of oxidative rancidity in dried fat emulsion products has been to use highly saturated fats, such as hydrogenated lauric-containing fats, as the fat component. However, the use of such fats is objectionable due to dietary concerns regarding such highly saturated fats, and difficulty in reconstituting the dried emulsion, particularly in cold water. Another approach has been to incorporate antioxidants, such a butylated hydroxyanisole and/or butylated hydroxytolune in the fat to inhibit the oxidative process. While the use of such antioxidants is effective in extending shelf life, the use of antioxidants adds significantly to the cost of the product and is objectionable to a number of consumers.

The present invention provides a method by which dried fat emulsion products can be produced having increased resistance to oxidation and the development of rancidity, particularly at elevated storage temperatures, without requiring the use of highly saturated fats or antioxidants. In the present invention, an aqueous dispersion of an edible fat or oil, a hydrophilic film forming material, and a carbohydrate, preferably a disaccharide, and water is emulsified to form a liquid oil-in-water emulsion concentrate having a solids content of about 25% to 75% in which the fat globules are encapsulated within a continuous layer of the film forming material. After the emulsion has been formed, a second portion of a hydrophilic film forming material is added to the emulsion concentrate in an amount substantially equivalent to the amount of the film forming material contained in the aqueous dispersion, to provide an additional coating layer of film forming material encapsulating the fat globules. This second portion of the film forming material preferably is added to the emulsion concentrate prior to drying, but may, if desired be added to the emulsion concentrate after drying, such as during instantizing of the dried emulsion concentrate. The film forming material used in this second addition may be the same as or different from the film forming material used in forming the initial aqueous dispersion.

It has been found that this second addition of film forming material is surprisingly effective in improving the resistance of dried fat emulsion products to oxidative deterioration and the development of rancidity as compared to dried fat emulsion products produced by the single-stage addition of the film former, even though the total amount of film forming material included in the dried emulsion product is the same in both cases. That is, when only about one-half of the amount of hydrophilic film forming material usually used in preparing a dried emulsion product by prior procedures is used in preparing the liquid emulsion concentrate, and the remaining one-half of the film former is added after the emulsion has been formed, the dried emulsion product resulting from the two stage addition of the film forming material has significantly greater resistance to oxidation at elevated temperatures than the product obtained when all of the film forming material is included at the time the emulsion is formed. Of course, the amount of film forming material included in the aqueous dispersion prior to formation of the emulsion must be sufficient to provide a continuous film encapsulating the fat globules in the emulsion.

Other edible ingredients usually used in the production of dried fat emulsion products may, if desired, also be included in the liquid emulsion concentrate, such as, for example, stabilizers, stabilizing salts, coloring, flavoring, preservatives, vitamins, minerals, and the like, depending on the intended use of the dried fat emulsion. The dried fat emulsion product may be characterized as comprising a matrix of water

soluble constituents having as the dispersed phase therein discrete small particles of fat.

In accordance with the present invention, an aqueous dispersion is formed by mixing together an edible fat, a hydrophilic film forming material, and a carbohydrate, preferably a disaccharide, with sufficient water to provide the dispersion with a solids content in the range of about 25% to 75%. Generally, any of the edible fats and oils, of both animal or vegetable source, normally used in dried fat emulsion products may be used. Fats and oils which may be used include unhydrogenated, partially or fully hydrogenated vegetable fats and oils such as, for example, cottonseed oil, coconut oil, corn oil, soybean oil, peanut oil, sunflower oil, palm kernel oil, and the like, including mixtures thereof, as well as tallow, lard, butterfat, and the like, having the flavor, melting point range, saponification value and other characteristics desired in the product in which the dried fat emulsion is to be used. The fat comprises the major solids component of the aqueous dispersion and may comprise up to 80% by weight of the solids content of the dispersion. If the fat used is solid or semi-solid at room temperature, it is melted prior to use in forming the aqueous dispersion.

The hydrophilic film forming material which may be used in the aqueous dispersion includes any of the edible film forming materials well known in the art as encapsulating agents in the production of dried emulsion products. Suitable materials have the properties of good film forming capability on oily surfaces, low hygroscopicity, low viscosity, and preferably, emulsion stabilizing properties so that a separate emulsifying agent need not be included in the aqueous dispersion. Examples of suitable film forming substances include proteinaceous hydrophilic colloids such as sodium or calcium caseinate, whey solids, non-fat milk solids, gelatin, and the like; hydrocolloid gums such as gum arabic, gum tragacanth, guar gum, carboxymethylcellulose, methylcellulose, and the like; gelatinized starch, dextrins and chemically modified dextrinized starches. In general, it is preferred to use sodium caseinate, gum arabic and/or chemically modified dextrinized starches as the film forming material in the present invention, for such materials have all of the properties set forth above, including good emulsion stabilizing properties, so that a separate emulsifier need not be included in the aqueous dispersion.

The amount of film forming material included in the aqueous dispersion should be sufficient to provide a continuous film encapsulating the fat globules in the emulsion. This amount will depend on the specific film former used, the amount of fat in the aqueous emulsion, and the desired size of the fat globules in the dried emulsion product. Thus, any ratio of fat to film former is suitable which will result in the formation of a stable emulsion in which the fat globules are encapsulated with a continuous film of the film forming material. As the ratio is increased, a point is reached where a stable emulsion cannot be formed because of the lack of an adequate amount of film former, resulting in coalescence, agglomeration and rising to the surface (creaming) of the fat particles prior to drying of the emulsion concentrate. This point will vary according to the film former used. For example, with a sodium caseinate-butterfat system, a fat to sodium caseinate ratio of about 15 to 1 in the aqueous dispersion appears to be the upper limit in providing a stable emulsion. Although this limit cannot be set forth for every conceivable system, it can be readily determined in a given system by slowly increasing the ratio until a stable emulsion can no longer be formed. The lower limit of this ratio is controlled only by cost considerations and the desired size of the fat globules in the emulsion. That is, as the ratio is decreased, the size of the fat globules decreases. The fat globules in the emulsion preferably have an average particle size of less than about 10 microns. In general, it is preferred that the fat to film former ratio in the aqueous dispersion be in the range of about 2:1 to 20:1. When sodium caseinate is used as the film forming material in both stages, it is preferred that the ratio of fat to caseinate in the aqueous dispersion be in range of about 5:1 to 15:1, with an equivalent amount being added to the liquid emulsion concentrate after formation of the emulsion.

If the film forming agent used does not have good emulsifying properties, a conventional emulsifier may be added to the aqueous dispersion to increase the ease of formation of the emulsion and to promote stability of the liquid emulsion concentrate to be dried. Emulsifiers which may be used are those which are approved for use in foods, such as mono- and diglycerides, glycerol mono-stearates, sorbitan esters of hexitol anhydrides, polyoxyethylene sorbitan esters of hexitol anhydrides, and combinations thereof. If an emulsifier is used, it is typically present in an amount of about 0.2% to 2.0% by weight of the solids content of the emulsion concentrate.

A carbohydrate material, preferably a disaccharide, such as sucrose, lactose, maltose, and mixtures thereof, is included in the aqueous dispersion in an amount of from about 3% to 35% by weight of the solids content of the aqueous dispersion in order to promote emulsion stability of the dried fat emulsion product.

Other edible materials usually used in the production of dried fat emulsion products for nutritive or organoleptic purposes, such as, for example, coloring, flavoring, vitamins, minerals, preservatives anti-foaming agents and the like, may if desired, also be included in the aqueous dispersion. If used, such

materials are usually present in small amounts.

In preparing the aqueous dispersion, the fat is melted (if a sold or semi-solid fat is used) by heating to about 55° C. to 65° C., and is added, with vigorous agitation, to hot water (65° C.-90° C.) in which the film forming material has been dispersed. The disaccharide is then added with agitation. If an emulsifier is used, it is usually added to the liquified fat. The amount of water is controlled to provide the aqueous dispersion with a solids content of about 25% to 75% by weight. The aqueous dispersion is then homogenized to an extent sufficient to provide an oil-in-water emulsion in which the fat globules have a desired particle size distribution, such as by homogenizing at about 140 to 210 Kg. per sq. cm. total pressure in a conventional two-stage homogenizer, with the fat globules in the emulsion being encapsulated in a layer of the film forming material.

After formation of the liquid emulsion concentrate, an additional quantity of hydrophilic film forming material is incorporated in the emulsion either prior to, during or subsequent to drying of the emulsion concentrate. The film forming material used in this second addition may be any of the film formers disclosed hereinabove, and may be the same as or different than the film former used in preparing the aqueous dispersion. The amount of film forming material in this second addition is substantially equivalent to the amount of film former contained in the aqueous dispersion. It is believed that this second addition of film forming material provides a second layer of film former encapsulating the fat globules which further protects the fat globules from oxidation, light, humidity and other deleterious conditions in storage. Such double encapsulated fat emulsion products exhibit better resistance to oxidation, particularly at elevated temperatures, than similar products prepared using an equivalent amount of film former in which all of the film forming material is added in a single step.

Thus, the second portion of the film forming material may be dispersed in a suitable quantity of water and added, with agitation, to the liquid emulsion concentrate, at any point prior to drying of the emulsion concentrate. Alternatively, the liquid emulsion concentrate may be dried, such as by spray drying, and the dried emulsion product instantized using water in which the second portion of the film former has been dispersed to wet the powder.

The dried emulsion product of this invention may be used in the production of any of the dry food systems in which dried emulsion products have been used in the past, such as, for example, dry cake mixes, powdered shortenings, dried coffee whiteners, topping mixes, sauce mixes, dried beverage mixes, and the like. Such products, when containing the dried emulsion product of the present invention, have improved resistance to oxidation and the development of rancidity, particularly at elevated temperatures.

The following specific examples are intended to illustrate more fully the present invention without acting as a limitation on its scope. As used herein, all percentages, parts, ratios and proportions are by weight and all temperatures are in °C. unless otherwise stated or otherwise obvious herefrom to one ordinarily skilled in the art.

Example 1

A dried fat emulsion product having the following formulation was prepared.

Ingredient	Percent
Fat (butterfat)	75.0
Sodium Caseinate	15.0
Lactose, crystalline	10.0

In preparing the dried emulsion from these ingredients, one-half of the sodium caseinate (i.e. 7.5g) was added to 92.5g of hot water (83° C.) and mixed well in a Waring blender. The fat was melted and added at a temperature of 60° C., with vigorous agitation, to the sodium caseinate dispersion, after which the lactose was added and the aqueous dispersion mixed until homogeneous. The resulting dispersion was then homogenized in a conventional two-stage homogenizer at 175 Kg./sq.cm. and 35 Kg./sq.cm. for the first and second stages respectively to form a liquid emulsion concentrate having a solids content of 50%. Since sodium caseinate has good emulsifying properties in addition to encapsulating and film forming capability, it was not necessary to include a separate emulsifying agent in the aqueous dispersion. The liquid emulsion concentrate was then pumped to a Bowen spray drier for drying. Just prior to introduction of the emulsion

concentrate to the spray dryer nozzles, a dispersion of 7.5g sodium caseinate in 92.5g hot water (83° C.) was added to the liquid emulsion concentrate in a 1:1 ratio, and the resulting emulsion was spray dried to produce a dried fat emulsion having a moisture content of less than about 3%. The dried emulsion was characterized as comprising a matrix of water soluble constituents having as the dispersed phase therein discrete small globules of fat, with the fat having been encapsulated in two stages.

Example 2

A dried fat emulsion product was prepared in accordance with the two-stage encapsulation process of the present invention and the properties of the product compared to those of a dried fat emulsion prepared by conventional single-stage encapsulation procedures. That is, a dried fat emulsion was prepared using the ingredients, amounts and procedure set out in Example 1, with the single exception that corn oil, rather than butterfat, was used as the fat component. The product produced by this two-stage encapsulation process was identified as Product A. Another dried emulsion product (Product B) was prepared using the same ingredients (i.e. corn oil, sodium caseinate, lactose and water) in the same amounts and the same procedure, with the exception that all of the sodium caseinate (15g) was added to the aqueous dispersion in a single step prior to formation of the emulsion. The oxidative stability of the dried products as well as that of unencapsulated corn oil (Product C) was then determined by the following test procedure.

A 10g sample of the dried emulsion product was introduced into a 500 ml flat bottom jar capped with a rubber septa, with glass cotton being used to disperse the product throughout the jar and maximize its exposure to oxygen. The jars were stored at 45° C., 50° C. and 60° C., and the headspace oxygen was determined for each jar by gas chromatography at two week intervals to determine the half-life of headspace oxygen in each jar, that is, the time required for the headspace oxygen in each jar to be reduced to 10.5% (half the original concentration). The results of this measurement are set out below in Table 1.

Table 1

Product Tested	Half-life (weeks)		
	45° C.	50° C.	60° C.
A	11	6.5	2.5
B	11	5.5	2.0
C	4.5	2.0	0.5

These test results show that the dried emulsion product produced in accordance with the two-stage encapsulation process of this invention has improved resistance to oxidation at elevated temperatures.

The particle size of Products A and B were determined using a Nicomp 270 Submicron Particle Sizer. Product B (the single-stage encapsulated product) had a bimodal particle diameter size distribution peaking at 600 and 140 nanometers, while Product A (the two-stage encapsulated product) had the same distribution with peaks at 1,125 and 240 nanometers.

Example 3

A dried fat emulsion product having the following formulation was prepared

Ingredient	Percent
Fat (butterfat)	80.0
Sodium Caseinate	10.7
Lactose	9.3

The procedure set out in Example 1 was used in preparing this product. That is, one-half (5.35g) of the sodium caseinate was included in an aqueous dispersion containing the fat, lactose and sufficient water to provide a liquid emulsion concentrate having a solids content of 50% by weight. The remaining 5.35g of sodium caseinate was dispersed in water and added to the emulsion prior to spray drying. The dried fat emulsion had excellent resistance to oxidation at elevated storage temperatures.

Example 4

Five samples of dried fat emulsion products were prepared and evaluated using gas chromatography to determine the differences in the extent of oxidation between the products. All of the samples were prepared using a formulation containing 75.0g corn oil, 15.0g film forming material, and 10.0g lactose. Product samples D, E and F were prepared using the two-stage encapsulation procedure of Example 1. In preparing sample D, gum arabic was used as the film forming material, with 7.5g of gum arabic being included in the aqueous dispersion, and 7.5g being added to the emulsion prior to spray drying. Sample E was prepared using sodium caseinate as the film forming material, with the caseinate being added in two stages of 7.5 g in each stage in accordance with the procedure of Example 1. Sample F was prepared by including 7.5g sodium caseinate in the aqueous dispersion, and adding 7.5g gum arabic to the emulsion concentrate prior to spray drying. Product samples G and H were prepared by a single stage encapsulation method in which all of the film former was included in the aqueous dispersion. That is, in sample G, 15g of sodium caseinate was added to the dispersion, and in Sample H, 15g of gum arabic was included in the aqueous dispersion.

The spray dried emulsion concentrates of each sample were evaluated by gas chromatography to determine the extent of oxidation of the samples. That is, 5g of the sample being evaluated were purged using a Tekmar 4000 Headspace Concentrator. The samples were purged with helium (zero grade) at a flow rate of 80 ml/min. for 20 minutes at 75° C. The flavor volatiles were trapped on a Tenax porous polymer trap. After completion of the purge cycle, the carrier gas (ultrapure hydrogen) transferred the compounds onto the head of a DB-5 fused silica column held in a Hewlett-Packard 5890 gas chromatograph. During a 5 minute desorb cycle the column was held at -20° C. After that time, the oven temperature was ramped to 200° C. at the rate of 8° C. per minute. Components eluting from the column were detected by flame ionization and the total volatiles eluted from the column for each sample was determined by calculating the total peak area of the gas chromatographic profile for each example. The results of these tests are set out in Table 2.

Table 2

Product Sample	Film Forming Material(s)	Total Volatiles
D	gum arabic/gum arabic	60,424,800
E	sodium caseinate/sodium caseinate	75,256,100
F	sodium caseinate/gum arabic	78,363,400
G	sodium caseinate	209,199,700
H	gum arabic	76,017,400

Since an increase in volatiles eluting from the column is indicative of increased fat oxidization, it is apparent that the two-stage encapsulation process of this invention provides increased resistance to oxidation. For example, Sample E (two-stage addition of sodium caseinate) had about 64% less volatiles than Sample G (one-stage addition of the same total amount of sodium caseinate), and Sample D (two-stage addition of

gum arabic) had about 20% less volatiles than Sample H (one-stage addition of the same amount of gum arabic).

Claims

1. The method of producing a dried fat emulsion product having long term stability against oxidation which comprises
emulsifying an aqueous dispersion containing an edible fat, a hydrophilic film forming material, a carbohydrate and water to form a stable liquid emulsion concentrate containing fat globules encapsulated with said film forming material,
adding to said liquid emulsion concentrate a hydrophilic film forming material in an amount substantially equal to that contained in the aqueous dispersion, and
drying said emulsion concentrate to provide a dried fat emulsion product.

2. The method defined in claim 1 in which the amount of film forming material included in the aqueous dispersion is sufficient to provide a continuous film encapsulating the fat globules.

3. The method defined in claim 1 in which the aqueous dispersion contains a ratio of fat to film forming material in the range of between about 2:1 to 20:1.

4. The method defined in claim 1 in which the fat comprises the major component of the solids content of the aqueous dispersion.

5. The method defined in claims 1 in which the film forming material is selected from the group consisting of proteinaceous hydrophilic colloids, hydrocolloid gums, gelatinized starch, dextrins and chemically modified dextrinized starches.

6. The method defined in claim 1 in which the film forming material added to the liquid emulsion concentrate is the same film forming material included in the aqueous dispersion.

7. The method defined in claim 1 in which the film forming material added to the liquid emulsion concentrate is different than the film forming material included in the aqueous dispersion.

8. The method defined in claim 5 in which the film forming material is selected from the group consisting of caseinates, gum arabic, chemically modified dextrinized starches, and combinations thereof.

9. The method defined in claim 8 in which the film forming material is sodium caseinate and is present in the aqueous dispersion in a ratio of fat to sodium caseinate of about 5:1 to 15:1.

10. The method defined in claim 1 in which the carbohydrate is a disaccharide which is present in an amount of from about 3% to 35% by weight of the solids content of the aqueous dispersion.

11. The method defined in claim 1 in which the fat globules in the liquid emulsion concentrate have an average particle size of less than about 10 microns.

12. The method defined in claim 1 in which the liquid emulsion concentrate has a solids content of about 25% to 75% by weight.

13. The method deferred in claim 1 in which the aqueous dispersion contains an emulsifying agent.

14. The method of producing a dried fat emulsion product having long term stability against oxidation which comprises
forming an aqueous dispersion containing an edible fat, a hydrophilic film forming material, a carbohydrate and sufficient water to provide an aqueous dispersion having a solids content of between about 25% to 75% by weight,
emulsifying said aqueous dispersion to form a stable liquid emulsion concentrate containing fat globules encapsulated with said film forming material,
drying said liquid emulsion concentrate to form a dried fat emulsion in which the fat globules have an average particle size of less than about 10 microns, and
instantizing the dried fat emulsion particles with an aqueous medium containing an amount of the hydrophilic film forming material substantially equal to that contained in the aqueous dispersion.

15. The product produced by the method of claim 1.

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(71) Applicant: **UNILEVER NV**
Burgemeester s'Jacobplein 1 P.O. Box 760
NL-3000 DK Rotterdam(NL)

(72) Inventor: **Freeman, Christopher Paul**
Meadow Bank Pavenham Road
Felmersham Bedford MK43 7EX(GB)
Inventor: **Jarvis, Robert Michael**
24 Spencer Court Station Road
Rushden Northants NN10 9TJ(GB)
Inventor: **Wilding, Peter**
113 Langham Road Raunds, Nr
Wellingborough Northants NN9 6LB(GB)

(74) Representative: **Butler, David John et al**
Unilever PLC Patents Division P.O. Box 68
Unilever House
London EC4P 4BQ(GB)

(54) **Dry solid compositions containing lipid.**

(57) A dry solid composition comprises from 70 to 95% by weight of lipid containing from 10 to 50% by weight free fatty acids, protected in sodium caseinate. The composition can be in free-flowing particulate form, and can be used as an ingredient in animal feedstuffs such as fish feeds. The composition can contain lipid-soluble components such as vitamins and carotenoid pigments.

EP 0 424 578 A1

DRY SOLID COMPOSITIONS CONTAINING LIPID

The present invention relates to compositions containing lipid and which are in dry, solid form.

Many human foodstuffs and animal feedstuffs contain substantial levels of lipid. Due to its essentially oily or sticky nature, the presence of such lipid can give rise to processing problems. Indeed there are instances, such as in feedstuffs for fish, where for nutritional reasons it would be desirable to include higher lipid levels but this is rendered difficult or impossible due to the ensuing processing problems. It is an object of the present invention to provide a composition containing a very high lipid level which is nevertheless in dry, free-flowing particulate form and from which the lipid does not readily leak. Such a composition could be used as a feedstuff in its own right, but will more usually be blended with other feed ingredients to make a composite product.

Many techniques have previously been proposed for making "protected lipids". In particular, the use of proteins such as blood as an encapsulating or protecting medium for lipids has been widely investigated. The results of such investigations feature in many publications and patent specifications. For example, in GB patent specification no. 2156305, we describe a method for making an encapsulated lipid wherein an emulsion of an acidic lipid (containing more than 20% free fatty acids) and a protein suspension (e.g. blood) is allowed to form a firm gel, which is then dried to produce the protected lipid product. GB 2156305 gives examples of products containing lipid levels of up to about 60% by weight.

It is clearly desirable that the product should contain the highest possible proportion of lipid consistent with satisfactory physical protection of the lipid still being obtained. It would be expected that if the proportion of lipid in the composition is raised, and hence the proportion of protein or other protective agent is reduced, the extent to which the lipid is protected will diminish. Indeed, if the process described in GB 2156305 is applied to emulsions containing more than 70% by weight lipid, the proportion of protein in the emulsion is insufficient to enable a firm gel to form. The resulting liquid emulsion cannot be dried in equipment in which the composition being dried experiences a tumbling action, which is the preferred technique disclosed in GB 2156305.

The present invention provides a dry solid proteinaceous composition, preferably in free-flowing particulate form, containing from 70-95% by weight lipid, which lipid contains not less than 10% and not more than 50% by weight free fatty acids, protected in caseinate, preferably sodium caseinate. Preferably the composition contains at least about 80% lipid.

We have found that sodium caseinate can provide very effective physical protection even at these very high lipid inclusion levels, whereas other proteins, such as blood and soya protein isolate, are significantly less effective.

Unsaturated lipids, such as fish oils, tend to be easily degraded by oxidation. An additional and remarkable advantage of the invention is that the caseinate-protected product exhibits considerable stability in this respect. The reason why caseinate confers this benefit is not fully understood.

The free fatty acid level in the lipid is critical, because if the free fatty acid level is greater than about 50% by weight, it is impossible to provide an adequately protected lipid even with sodium caseinate. Similarly, if the free fatty acid level is below about 10% by weight of the lipid, significant leakage of the lipid from a caseinate-protected product can occur.

The invention also provides a process wherein a liquid emulsion of lipid, which lipid material contains from 10% to 50% by weight free fatty acids, in an aqueous solution containing not less than about 5% by weight of caseinate, is dried.

Preferably the free fatty acid content of the lipid is at least 20%, and more preferably at least 30%. We have found that an ideal level of free fatty acids in the lipid is about 40% by weight. Preferably the desired level of free fatty acids is achieved by blending different oils, such as neutral oil, e.g. whole fish body oil, with acid oil, e.g. distilled fish acid oil.

The liquid emulsion can be dried by a range of techniques, it is preferable to use fluid bed drying, spray drying or drum (film) drying.

In a particularly preferred embodiment of the invention, the lipid is fish oil. The fish oil can comprise a blend of commercially-available oils, such as whole fish body oil, fish acid oil and fish acid oil distillate. Other oils, such as soyabean oil and sunflower oil, can also be used.

A typical process according to the invention will involve homogenising the acidic lipid and an aqueous caseinate solution together, at a temperature of at least about 50 °C to ensure that the lipid is fully liquid and the caseinate solution is not too viscous. The resulting emulsion is then dried.

Sodium caseinate is available commercially as a dry solid, and can be dissolved in water to provide the necessary solution. In general, the solution should contain from about 10% to about 20% by weight at caseinate. Alternatively, it is possible to use caseinate solution from a milk processing

plant, thus avoiding the inherent cost of starting the process from a dried material to which water must be returned and then removed again. Preferably the pH of the solution should be at least about 6.5 but not greater than about 6.8.

Preferably, the lipid should be essentially free from traces of soaps or mineral acids (usually hydrochloric acids or sulphuric acid) which can interfere with the protective properties of the caseinate. Commercially-available oils, such as fish acid oil, are sometimes contaminated with such materials, and care should be taken as far a possible to ensure that the supply of lipid has a high degree of purity in this respect.

The invention has particular relevance to the manufacture of protected lipids for use in fish feeds.

An added advantage of the compositions of the invention is that they can be used as a vehicle for lipid-soluble ingredients, such as vitamins and carotenoid pigments such as astaxanthin, which are valuable components of feeds for creatures such as fish. Further aspects of the invention are feedstuff for fish comprising caseinate-protected lipid together with other nutrient materials, such as fish meal and cereals. Preferably such feedstuffs are in the form of extruded pellets, and it is an advantage of the invention that the caseinate-protected lipid can be blended with other feed ingredients and pelleted without the physical protection of the lipid seriously being affected by the processing conditions. The invention also includes the rearing of fish on a diet incorporating caseinate-protected lipid. The invention particularly provides a method of rearing salmonid fish, such as salmon or trout, on a diet incorporating caseinate-protected lipid containing a red-coloured carotenoid pigment, especially astaxanthin.

The following example illustrates the manufacture of a composition in accordance with the invention.

Example 1

2.4kg dried sodium caseinate was added slowly into 13.6 litres of water at 70° C, with constant stirring. The mixture was then vigorously agitated for a period of 2 minutes, using an industrial stirrer, to effect complete solution. A blend of fish oil fatty acid distillate (3.6kg), neutralised fish oil (5.4kg) and ethoxyquin antioxidant (9g) at 70-80° C was then added slowly, with constant stirring, to the caseinate solution also at 70-80° C. The mixture was then homogenised at the same temperature using a high-pressure ultrasonic homogeniser at a pressure of 14-16 bar. The homogenate was then dried using a fluid-bed drier, to give a free-flowing particulate composition which could be handled without leaving any oil residue.

Example 2

A protected lipid product according to the invention was prepared by the procedure in Example 1, containing 20% sodium caseinate and 80% of a 60:40 blend of neutralised marine oil, and fish oil fatty acid distillate containing 0.1% ethoxy quin anti-oxidant. The product was stored in bulk in a paper sack, and also as a number of small samples heat-sealed in plastic bags. The bags and sack were placed in cardboard boxes to keep out light and stored at ambient temperature over 12 months. Samples were regularly taken for analyses, and the composition of the lipid determined by GLC. The samples in plastic bags were analysed and discarded once opened. Fatty acids were methylated using a toluene, methanol, sulphuric acid reflux, and the fatty acid methyl esters were analysed on a wide bore capillary column. Using this method, the level of polyunsaturated fatty acids in the fish oil was monitored throughout the storage trial. Particular attention was given to the level of C20:5 and C22:6 acids. These polyunsaturated acids are very important constituents of fish oil, and any chemical degradation of these acids significantly lowers the nutritional value of the oil and leads to unpleasant rancidity characteristics.

Throughout the period of the trial, the percentage level of both of these important polyunsaturated fatty acids remained essentially constant in the product. These results are shown graphically in the accompanying drawing (Figure 1). Under similar storage circumstances, commercial fish meal deteriorates rapidly and even after a period of only six months, it would usually be regarded as unusable. After six months, the percentage level of essential polyunsaturated fatty acids in commercial fish meal would have fallen dramatically.

Claims

1. A dry solid proteinaceous composition containing lipid, wherein the lipid comprises from 70 to 95% by weight of the composition, the lipid contains from 10 to 50% by weight free fatty acids, and the protein is caseinate.
2. A composition according to claim 1, wherein the lipid comprises at least about 80% by weight of the composition.
3. A composition according to claim 1 or claim 2, wherein the protein is sodium caseinate.
4. A composition according to any one of the preceding claims, wherein the lipid contains at

least 20% by weight free fatty acids.

5. A composition according to claim 3, wherein the lipid contains at least 30% by weight free fatty acids.

6. A composition according to any one of the preceding claims, wherein the lipid contains about 40% by weight free fatty acids.

7. A composition according to any one of the preceding claims, wherein the lipid is fish oil.

8. A composition according to any one of claims 1 to 7, additionally incorporating one or more lipid-soluble feedstuff ingredients.

9. A composition according to claim 8, incorporating a vitamin.

10. A composition according to claim 8, incorporating a carotenoid pigment.

11. A composition according to claim 10, wherein the pigment is astaxanthin.

12. An animal feedstuff comprising a composition according to any one of claims 1 to 11, blended with other nutrient materials.

13. A feedstuff for fish comprising a composition according to any one of claims 1 to 11, blended with other nutrient material such as fish meal and cereals.

14. A feedstuff according to claim 12 or claim 13, in the form of extruded pellets.

15. A process for the preparation of a dry, free-flowing protected lipid composition, wherein a liquid emulsion of lipid, which lipid contains from 10 to 50% by weight free fatty acids, in an aqueous solution containing not less than about 5% by weight of caseinate, is dried.

16. A process according to claim 15, wherein the caseinate is sodium caseinate.

17. A process according to claim 15 or claim 16, wherein the lipid contains at least 20% by weight free fatty acids.

18. A process according to claim 17, wherein the lipid contains at least 30% by weight free fatty acids.

19. A process according to any one of claims 15 to 18, wherein the lipid contains about 40% by weight free fatty acids.

20. A process according to any one of claims 15 to 19, wherein the lipid is fish oil.

21. A process according to any one of claims 15 to 20, wherein the emulsion is dried by fluid bed drying or spray drying or drum drying.

22. A process according to any one of claims 15 to 21, wherein the acidic lipid and the caseinate solution are homogenised together at a temperature of at least about 50° C, and then dried.

23. A process according to any one of claims 15 to 22, wherein the aqueous solution contains from about 10% to about 20% by weight caseinate.

24. A process according to any one of claims 15 to 23, wherein the pH of the aqueous solution is at least about 6.5.

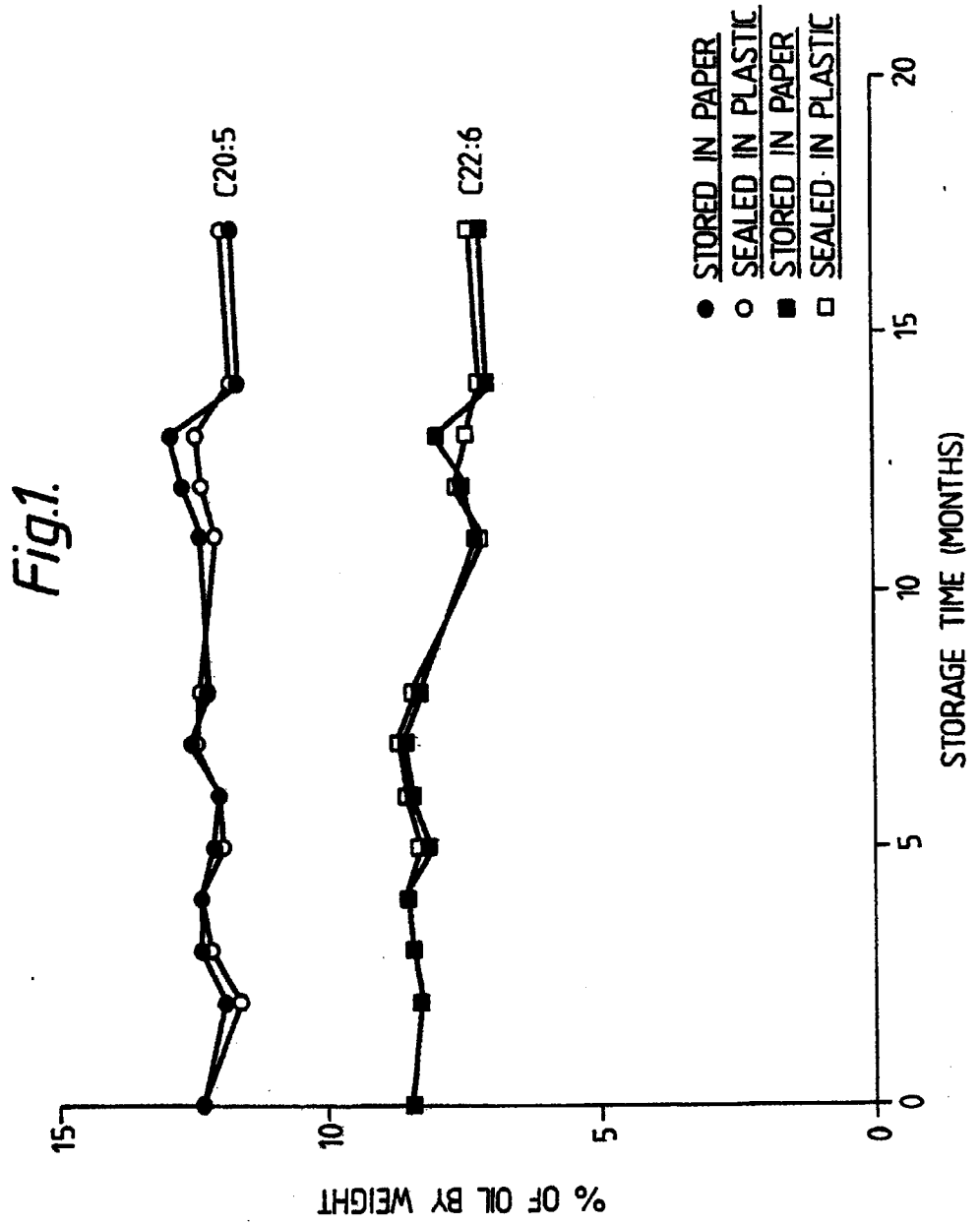
25. A process according to any one of claims 15 to 24, wherein the pH of the aqueous solution is not greater than about 6.8.

26. A composition according to any one of claims 1 to 14, in free-flowing particulate form.

27. Rearing of fish on a diet incorporating a composition according to any one of claims 1 to 11.

28. Rearing of salmonid fish, such as salmon or trout, on a diet incorporating a composition according to claim 10 or claim 11.

Fig.1.


C20:5
C22:6
STORED IN PAPER
SEALED IN PLASTIC
STORED IN PAPER
SEALED IN PLASTIC
% OF OIL BY WEIGHT
STORAGE TIME (MONTHS)
0
5
10
15
20

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 31 0874

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	GB-A-2 031 937 (BALFOUR MANUFACTURING CO.) * Claims 1-4,6,8,9,17,23,24; page 2, lines 78-85 *	1-3,12, 14-16, 21-26	A 23 D 9/00 A 23 J 1/20 A 23 K 1/00
X	WO-A-8 802 221 (KABIVITRUM AB) * Claims 1,3,5,10,12; page 2, lines 1-17; page 3, lines 1-30 *	1,7-9, 12,15, 20-22, 26	
X	JOURNAL OF THE SCIENCE OF FOOD AND AGRICULTURE, vol. 31, no. 5, 1980, pages 439-447, Society of Chemical Industry, Barking, GB; J.L. CLAPPERTON: "The extent of hydrogenation of two formaldehyde-treated spray-dried mixtures of soya bean oil and casein fed to sheep" * Page 439, abstract; page 440, last paragraph - page 441, first paragraph *	1-3,15, 16,21, 26	
D,A	GB-A-2 156 305 (UNILEVER PLC) * Claims 1-4,7,8,10,11,13-19,21; page 1, lines 45-47; page 2, lines 17-20,36-38 *	1,4-9, 12-15, 17-21, 26,27	TECHNICAL FIELDS SEARCHED (Int. Cl.5) A 23 D A 23 J A 23 K
A	GB-A-1 062 423 (NIPPON YUSHI K.K.) * Claims 1,4,9; page 1, lines 40-45,84 - page 2, line 24; page 2, lines 69-70; example 2 *	1,2,7, 15,20-22,26	
A	GB-A- 820 995 (UNILEVER) * Claims 1,6,9,11,12; page 2, lines 25-30 *	1,2,15, 21,26	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23-04-1990	DEKEIREL M.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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(71) Applicant: **UNILEVER PLC**
Unilever House Blackfriars P.O. Box 68
London EC4P 4BQ(GB)
(84) **GB**

Applicant: **UNILEVER NV**
Burgemeester s'Jacobplein 1 P.O. Box 760
NL-3000 DK Rotterdam(NL)
(84) **BE CH DE DK ES FR GR IT LI NL SE AT**

(72) Inventor: **Freeman, Christopher Paul**
Unilever Research Colworth Lab, Colworth House
Sharnbrook, Bedford MK44 1LQ(GB)
Inventor: **Jarvis, Robert Michael**
24 Spencer Court, Station Road,
Rushden, Northants NN10 9TJ(GB)

(74) Representative: **Butler, David John et al**
Unilever PLC Patents Division P.O. Box 68
Unilever House
London EC4P 4BQ(GB)

(54) Dry solid compositions containing lipid.

(57) A dry free-flowing particulate composition containing from 70-95% by weight lipid is made by drying a liquid emulsion of lipid in an aqueous solution of sodium caseinate an dextrin having a dextrose equivalent of less than 10, preferably 2 - 3. The dry composition can be used as a vehicle for lipid soluble dietary components such as vitamins and carotenoids, and can protect unsaturated oils against oxidative deterioration.

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DRY SOLID COMPOSITIONS CONTAINING LIPID

The present invention relates to compositions containing lipid and which are in dry solid form.

The present invention provides a dry solid composition, preferably in free-flow particulate form, containing lipid protected in a combination of caseinate and starch.

Preferably the caseinate is sodium caseinate.

The starch can be unmodified or modified. Blends of starches can be used. Suitable modified starches include chemically modified starches and hydrolysed starches. Hydrolysed starches (dextrins) are most preferred. Dextrins having a dextrose equivalent of less than about 10, and more especially of about 6 or less, are preferred. Dextrins of dextrose equivalent in the range of about 2 to about 3 are particularly suitable.

The ratio of caseinate to starch can vary widely. Subject to certain constraints on the nature of the lipid (detailed below), it is possible to make a protected lipid composition in accordance with the invention in which caseinate provides almost the whole of the protective medium. We have observed that caseinate has a surprising ability to protect unsaturated oils against oxidative deterioration, and this property can be exploited in a product containing unsaturated lipids (such as fish oils) if the caseinate proportion in the protective medium is very high.

However, for economic reasons, it is highly desirable that caseinate should not comprise a high proportion of the protective medium. An important aspect of the invention is the use of a combination of caseinate and dextrin as a protective medium, in which the dextrin comprises the major component in the protective medium.

A combination of caseinate and dextrin is particularly beneficial because dextrins are highly water-soluble and in solution exhibit low viscosity. By the use of a combination of caseinate and dextrin, low moisture emulsions with lipids can be made and the product of the invention can be produced with economically low drying costs. If raw starches or modified starches which have not been hydrolysed are used, higher moisture levels and greater drying costs are involved.

It is an object of the invention to provide a dry solid composition containing a high level of lipid (preferably at least 70% by weight of the dry product), which is sufficiently robust that the product can be blended with feed materials and processed (eg. by pelleting) without the protective structure of the product being broken down to release the lipid. The combination of caseinate and dextrin enables such a robust product to be made. Indeed, such products can be made with more than 80% by weight lipid in the final dry solid product. A particularly preferred embodiment of the invention is a dry solid composition preferably in free-flowing particulate form containing from 70-95% by weight lipid, protected in a combination of caseinate and dextrin.

Preferably the caseinate comprises at least about 3% by weight of the final dry product.

The free fatty acid level in the lipid may be critical if the caseinate forms a high proportion of the protective medium: if the free-fatty acid level is greater than about 50% by weight, it is impossible to provide an adequately protected lipid with sodium caseinate alone. If the free fatty acid level is below about 10% by weight of the lipid, significant leakage of the lipid can occur from a protected product based primarily on caseinate.

The percentage of caseinate in the protective medium (caseinate plus starch) in the final dry product, is preferably at least about 10%, and more preferably at least about 15%, by weight. Thus, for example, an ideal product in accordance with the invention may comprise about 3% caseinate, about 17% dextrin and about 80% of neutral oil such as neutralised marine oil. For vegetable oils, the caseinate level is preferably slightly higher. For example, in a final dry product based primarily on soya oil, the caseinate level is preferably not less than about 20% by weight of the protective medium, and in a final dry product based primarily on coconut oil the caseinate level is preferably not less than about 25% by weight of the protective medium. If the lipid is acidic, for example commercial fish acid oil which will usually contain at least 10% by weight free-fatty acids, a higher proportion of caseinate should be used. If the free-fatty acid level in the lipid is 10% or greater, it is preferable that the percentage of caseinate in the protective medium in the final dry product is at least about 30%, and more preferably at least about 35%, by weight. For example, a product according to the invention can be made containing about 7% caseinate, about 13% dextrin and about 80% fish acid oil.

The invention also provides a process wherein a liquid emulsion of lipid in an aqueous solution containing caseinate and dextrin, is dried.

The liquid emulsion can be dried by a range of techniques, it is preferable to use fluid bed drying, spray drying or drum (film) drying. An especially preferred process involves spray drying followed by agglomeration, eg. using a fluidised bed.

In a particularly preferred embodiment of the invention, the lipid is fish oil. The fish oil can comprise a blend of commercially-available oils,

such as whole fish body oil, fish acid oil and fish acid oil distillate. Other oils, such as soyabean oil and sunflower oil, can also be used.

A typical process according to the invention will involve homogenising the lipid and an aqueous caseinate/starch solution together, at a temperature of at least about 50 °C to ensure that the lipid is fully liquid and the solution is not too viscous. The resulting emulsion is then dried.

Sodium caseinate is available commercially as a dry solid, and can be dissolved in water to provide the necessary solution. In general, the solution should contain from about 10% to about 20% by weight at caseinate. Alternatively, it is possible to use caseinate solution from a milk processing plant, thus avoiding the inherent cost of starting the process from a dried material to which water must be returned and then removed again. For protective media containing caseinate levels of 50% or more, preferably the pH of the solution is at least about 6.5 but not greater than about 6.8.

Preferably, the lipid should be essentially free from traces of soaps or mineral acids (usually hydrochloric) acids or sulphuric acid) which can interfere with the protective properties of the caseinate. Commercially-available oils, such as fish acid oil, are sometimes contaminated with such materials, and care should be taken as far a possible to ensure that the supply of lipid has a high degree of purity in this respect.

The invention particular relevance to the manufacture of protected lipids for use in fish feeds.

An added advantage of the composition of the invention is that they can be used as a vehicle for lipid-soluble ingredients, such as vitamins and carotenoid pigments such as astaxanthin, which are valuable components of feeds for creatures such as fish. Further aspects of the invention are feedstuff for fish comprising the protected lipid together with other nutrient materials, such as fish meal and cereals. Preferably such feedstuffs are in the form of extruded pellets, and it is an advantage of the invention that the protected lipid can be blended with other feed ingredients and pelleted without the physical protection of the lipid seriously being affected by the processing conditions. The invention also includes the rearing of fish on a diet incorporating the protected lipid. The invention particularly provides a method of rearing salmonid fish, such as salmon or trout, on a diet incorporating the caseinate/starch protected lipid containing a red-coloured carotenoid pigment, especially astaxanthin.

The following example illustrates the manufacture of a composition in accordance with the invention.

Example

150 grams sodium caseinate and 850 grams of commercially-available dextrin (D.E. 2.5) were dissolved, with constant stirring, in 2143 grams of water at 70 °C. The mixture was then vigorously agitated (while avoiding aeration) for a period of 2 minutes using an industrial stirrer to effect complete solution. 4kg of neutralised marine oil containing 0.1% ethoxyquin at 70 °C was slowly added to the solution with vigorously stirring to form a stable pre-mix. The pre-mix was passed four times through a piston homogeniser at 1500 to 1700 p.s.i. to produce a stable emulsion. The emulsion was spray-dried at an inlet temperature of 200 - 220 °C and an outlet temperature of 85 - 95 °C. The product was a free-flowing particulate composition which could be handled without leaving any oil residue.

Claims

1. A dry solid free-flowing particulate composition comprising lipid protected in a combination of caseinate and starch.
2. A composition according to claim 1 wherein the caseinate is sodium caseinate.
3. A composition according to claim 1 or claim 2, wherein the starch is hydrolised starch.
4. A composition according to claim 3, wherein the starch is a dextrin having a dextrose equivalent of less than about 10.
5. A composition according to claim 4, wherein the dextrose equivalent is about 6 or less.
6. A composition according to claim 4, wherein the dextrose equivalent is in the range of about 2 to about 3.
7. A composition according to any one of the preceding claims, wherein the starch comprises the major component in the protective medium.
8. A composition according to any one of the preceding claims, containing from 70 - 95% by weight lipid.
9. A composition according to any one of the preceding claims which comprises at least about 3% by weight caseinate.
10. A composition according to any one of the preceding claims, wherein the caseinate comprises at least about 10% by weight of the protective medium.
11. A composition according to claim 10, wherein the caseinate comprises at least about 15% by weight of the protective medium.
12. A composition according to any one of the preceding claims, wherein the lipid comprises neutralised marine oil.
13. A composition according to any one of claims 1

to 11, wherein the lipid is acidic and the caseinate comprises at least about 30% by weight of the protective medium.

14. A composition according to claim 13, wherein the lipid is fish acid oil.

15. A composition according to any one of the preceding claims, containing a lipid-soluble feed ingredient.

16. A composition according to claim 15, containing a lipid-soluble vitamin.

17. A composition according to claim 15, containing a carotenoid pigment.

18. A composition according to claim 17, containing astaxanthin.

19. Use of a composition according to any one of the preceding claims as a feed additive.

20. Use of a composition according to any one of claims 1 to 14 as a vehicle for a lipid-soluble ingredient.

21. Use of a composition according to any one of claims 1 to 14 to protect unsaturated oil against oxidative deterioration.

22. A feedstuff incorporating a composition according to any one of claims 1 to 18.

23. A feedstuff for fish incorporation a composition according to any one of claims 1 to 18.

24. A process for the preparation of a composition according to any one of claims 1 to 18, wherein a liquid emulsion of lipid in an aqueous solution of caseinate and dextrin is dried.

25. A process according to claim 24, involving spray-drying.

26. A process according to claim 25, wherein the spray-drying is followed by agglomeration.

27. A process according to claim 26, wherein the agglomeration is conducted using a fluidised bed.

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(71) Applicant: **NESTEC S.A.**
1800 Vevey (CH)

(72) Inventor: **Sievert, Birgit**
1066 Epalinges (CH)

(74) Representative: **Vergani, Diego**
Nestec S.A.2
Avenue Nestlé 55
1800 Vevey (CH)

(54) Cereal based food product comprising DHA

(57) The invention relates to a cereal based food product, preferably shaped as a bar, having a water activity between 0.2 and 0.4 and comprising encapsulated DHA and one or more citrus flavors. The food product according to the present invention has no off-taste and odor.

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Description

Field of the Invention

[0001] The present invention relates to cereal based food products comprising DHA (decosahexanoic acid), without fish off-tastes and odors.

Background of the invention

[0002] Docosahexaenoic acid (DHA), a long-chain omega-3 polyunsaturated fatty acid, is important throughout pregnancy and lactation for the health of both the mother and her fetus/infant. A recent National Institutes of Health workshop of fatty acid experts recognizing the importance of maternal DHA intake recommended 300mg/day of DHA as adequate intake for pregnant and lactating women. Some of the research prompting this recommendation includes:

- Maternal DHA levels decline significantly in the last trimester, the period during which much maternal DHA is transferred from mother to fetus,
- In preterm infants, DHA levels in the umbilical artery wall, which reflect the long-term fetal DHA status, have been positively correlated to newborn head circumference, weight and length,
- In a dietary study of 119 pregnant or lactating women in the United States, the average intake of DHA was 54mg/day, only 18% of that recommended by experts. Less than 2%of these women met the recommended DHA average intake,
- Increasing maternal DHA intake during pregnancy, through diet or supplements, increases maternal and newborn DHA levels,
- DHA was cited as the likely component of breast milk affecting significant increases in cognitive outcomes of breast-fed infants through the first eighteen years of life,
- Even up to two years of age, breast-fed infants have higher skeletal muscle DHA and lower blood glucose levels than formula-fed infants,
- At 6 weeks postpartum, maternal DHA levels remain lower than levels of non-pregnant women,
- Reported DHA levels in breast milk of American women 15-26 are lower than what is recommended for formula-fed infants by a joint expert committee of the World Health Organization and the Food and Agriculture Organization,
- During lactation, increasing maternal intake of DHA with dietary supplements improves maternal, breast milk and infant DHA levels.

[0003] To answer this well known and health-concerning problem, some companies have launched products, such as cereal bars, containing DHA. For example, Arkopharma Laboratories have launched snack bars (Gouter Vitalité®) for pregnant women, enriched with vitamins, minerals, essential nutrients, calcium, zinc, iron, magnesium, phosphorous, 10 vitamins and folic acid. Each bar contains 65 calories and it is recommended that one to two should be eaten each day. The ingredients include, among others, rice flour, corn flour, vegetable fatty matter, calcium phosphate, saccharose, salt, magnesium oxide, flavoring, vitamin C, DHA, vitamin E, vitamin PP, antioxidant (palmitate ascorbate) and natural tocopherols.

[0004] WO 0072842 to KV Pharmaceutical Company discloses a composition comprising a first fatty acid such as linoleic or linolenic acid in a range of 10 to 1000 mg, a second fatty acid such as DHA in a range of 10 to 1000 mg, vitamin C or a derivative thereof (i.e. ascorbate) in a range of 25 to 500 mg, and further vitamins and minerals. The composition disclosed may be in the form of any acceptable dosage forms, such as health bars, and may be in the form of cereals.

[0005] However, DHA is well known to have a very strong odor and off-taste of fish oil, rejected by the consumer. Numerous attempts have been made to mask the off taste of fish oil or DHA. For example, EP 296117 to Warner-Lambert Co proposes to render unpleasant tasting edible oil palatable by adding a sensory masking agent. The sensory masking agent can be a taste-masking agent such as anethole, dihydroanethole, eugenol, vanillin, ethylvanillin, ethyl maltol. It can also be an artificial or natural odor masking agent, such as lime, lemon, orange, pineapple, grapefruit, cinnamon, clove, bay, allspice, anise, wintergreen, spearmint, benzaldehyde or cherry.

[0006] Furthermore, the use of ascorbic acid or its derivatives is a well-known method for preventing oxidation of fish oil or DHA. JP 07107938 to Saneigen FFI KK discloses an emulsion composition for food, pharmaceuticals, cosmetics and pet food containing docosahexanoic acid and vitamin C, for long-term storage, avoiding odor change or rapid oil oxidation of e.g. purified palm oil.

[0007] However, none of the prior attempts to mask or to remove the strong off-tastes and odors of DHA have been successful, and edible products containing DHA are still rejected by the consumer because of this long lasting, strong and very unpleasant fish off-taste.

Summary of the invention

[0008] We have now surprisingly found that it is possible to obtain cereal based food products comprising DHA, even at high concentrations, without off-taste. The cereal based food product according to the invention has a water activity between 0.2 and 0.4 and comprises encapsulated DHA and one or more citrus flavors.

Detailed description of the invention

[0009] We have found that the off-tastes and odors of the DHA contained in the cereal based food product according to the invention completely disappear, and this applies for relatively small contents of DHA, such as 100 mg DHA per 100 grams of cereal based food product, for example, as well as for very high contents of DHA, such as 1300 mg and even up to 2200 mg or more DHA per 100 grams of cereal based food product. This allows to strongly decrease the amount of product the intended consumer has to ingest daily to meet the recommended intake of about 600 mg DHA/day. As the intended consumer is usually a pregnant or lactating woman who, in most cases, have to look closely after her diet, and especially after her daily calorie intake, eating a small number of cereal based food product, and still ingesting a high amount of DHA, is a good answer to her needs.

[0010] According to the present invention, the flavors are preferably extracted from the Rutaceae family (Sapindales order), and most preferably from the Citrus genus. This includes, according to the invention, flavors from species *Citrus aurantifolia (Christm.)* Swingle (lime), *Citrus aurantium L.* (sour orange), *Citrus limetta Risso* (bitter orange), *Citrus limon* (L.) Burm. F. (lemon), *Citrus limonia* Obsbeck (pro sp.) (mandarin lime), *Citrus maxima* (Burm. F.) Merr (shaddock), *Citrus medica* L. (citron), *Citrus paradisi* Macfad. (pro sp.) (grapefruit), *Citrus reticulata* Blanco (tangerine), and *Citrus sinensis* (L.) Osbeck (sweet orange). This aspect of the invention can be understood as comprising flavors of one or more of the aforementioned species.

According to the present invention, the flavors are preferably chosen among the group consisting of orange flavor, lemon flavor, grapefruit flavor and mixtures thereof.

Examples of particularly suitable flavors are lemon tertrarome liquid 987317 (catalogue number) and orange tetrarome liquid 987431 (catalogue number), both by Firmenich SA, Geneva, Switzerland.

[0011] The citrus flavor content of the cereal based product according to the present invention may be comprised between 0.01 to 0.20 wt-%, preferably 0.07 to 0.17 wt-%, most preferably 0.10 to 0.15 wt-%, and in a most preferred embodiment 0.13 wt-%. The term "wt-%" has to be understood, throughout the present patent application, as the amount (in grams) of a certain ingredient per 100 g of the final product.

[0012] The citrus flavors are preferably added into the cereal based food product either in powdered form or associated with alcohol. They can also be added associated with water or water-containing liquids as far as the water activity value of the final cereal based product is maintained between 0.2 and 0.4.

[0013] It has to be understood that in addition to the citrus flavors, other flavors can be added such as, for example, honey flavor, fruit flavor, chocolate flavor, caramel flavor, nut flavor, almond flavor, yogurt flavor and mixtures thereof.

[0014] Water activity can be defined as the ratio of the water vapor pressure of a product to the vapor pressure of pure water at the same temperature. If the target water activity is exceeded, free water will migrate into the cereals. Moisture transfer may generate loss of the crispy texture, a mat appearance, the development of stale notes/off-tastes and may accelerate fat oxidation reactions and, therefore, the cereal based product will not be shelf stable. The cereal based food product according to the present invention shows a water activity comprised between 0.2 and 0.4, preferably 0.25 to 0.38, most preferably 0.30 and 0.35 and, in a most preferred embodiment,0.33.

[0015] DHA must be encapsulated into an edible component forming a closed barrier between DHA and the rest of the product or the atmosphere. Accordingly, encapsulating DHA in a matrix is not sufficient, for the purpose of the present invention. Examples of encapsulation fulfilling the requirements of the present invention are encapsulations in sugar, proteins, fats glycerol, or a mixture of monosaccharides and alcohol such as propanetriol, for example. According to a preferred embodiment of the present invention, the effective amount of DHA can vary up to 2200 milligrams of DHA per 100 grams of cereal based food product. The effective amount of DHA is defined on a 100% basis and, therefore, it merely includes the amount of pure DHA, and not that of pure DHA plus the encapsulating material.

[0016] It is also possible to add some other components to the cereal based food product according to the invention in order to further improve the organoleptic and/or nutritional characteristics of the product. These components may be chosen among glycerol, honey, prebiotics, probiotics, antioxidants, oxygen absorbers and others.

[0017] "Prebiotic" means a substance or compound which is fermented by the intestinal flora of a pet and/or a human and hence promotes the growth or development of bifido- and lactic-bacteria in the gastro-intestinal tract at the expense of pathogenic bacteria.

Suitable prebiotics include oligosaccharides, such as inulin and its hydrolysis products commonly known as fructooligosaccharides, galacto-oligosaccarides, xylooligosaccharides or oligo derivatives of starch. The prebiotics may be provided in any suitable form. For example, the prebiotic may be provided in the form of plant material which contains

the prebiotic. Suitable plant materials includes asparagus, artichokes, onions, wheat or chicory, or residues of these plant materials. Alternatively, the prebiotic may be provided as an inulin extract. Extracts from chicory are particularly suitable. Suitable inulin extracts are commercially available.

[0018] "Probiotic micro-organism" means a micro-organism which beneficially affects a host by improving its intestinal microbial balance (Fuller, R; 1989; J. Applied Bacteriology, 66: 365-378).

The probiotic micro-organism may be selected from one or more micro-organisms suitable for animal and/or human consumption and which is able to improve the microbial balance in the intestine. Examples of suitable probiotic micro-organisms include yeasts such as *Saccharomyces, Debaromyces, Candida, Pichia* and *Torulopsis,* moulds such as *Aspergillus, Rhizopus, Mucor,* and *Penicillium* and *Torulopsis* and bacteria such as the genera *Bifidobacterium, Bacteroides, Clostridium, Fusobacterium, Melissococcus, Propionibacterium, Streptococcus, Enterococcus, Lactococcus, Staphylococcus, Peptostrepococcus, Bacillus, Pediococcus, Micrococcus, Leuconostoc, Weissella, Aerococcus, Oenococcus* and *Lactobacillus.* Specific examples of suitable probiotic micro-organisms are: *Saccharomyces cereviseae. Bacillus coagulans, Bacillus licheniformis, Bacillus subtilis, Bifidobacterium bifidum, Bifidobacterium infantis, Bifidobacterium longum, Enterococcus faecium, Enterococcus faecalis, Lactobacillus acidophilus, Lactobacillus alimentarius, Lactobacillus casei* subsp. *casei, Lactobacillus casei Shirota, Lactobacillus curvatus, Lactobacillus delbruckii* subsp. *lactis, Lactobacillus farciminus, Lactobacillus gasseri, Lactobacillus helveticus, Lactobacillus johnsonii, Lactobacillus reuteri, Lactobacillus rhamnosus (Lactobacillus* GG), *Lactobacillus sake, Lactococcus lactis, Micrococcus varians, Pediococcus acidilactici, Pediococcus pentosaceus, Pediococcus acidilactici, Pediococcus halophilus, Streptococcus faecalis. Streptococcus thermophilus, Staphylococcus carnosus,* and *Staphylococcus xylosus.* The probiotic micro-organisms may be in powdered, dried form; especially in spore form for micro-organisms which form spores. Further, if desired, the probiotic micro-organism may be encapsulated to further increase the probability of survival; for example in a sugar matrix, fat matrix or polysaccharide matrix.

[0019] Antioxidants inhibit oxidation by molecular oxygen, and are commonly used to delay fat staling. Primary antioxidants act by blocking free radicals such as peroxide radicals, which are responsible for the first oxidation step of unsaturated fatty acids. Secondary antioxidants act either by chelating metallic ions, which are the oxidation catalysts, or by inhibiting lipoxygenases. Suitable antioxidants are, for example, L ascorbic acid, 1 sodium ascorbate, 1 calcium ascorbate, ascorbyle palmitate, alpha, delta or gamma tocopherols, BHA (butylhydroxyanisol), BHT (butylhydroxytoluene), lactic acid, sodium, potassium or calcium lactates, citric acid, and more generally anti-oxygens E 300 to E 309, E 311 and E 312, E 320 to E 322, E 220 to E 224, E 226, E 270, E 325 to E 327, E 330 to 341, and E 472c (European Economic Community numerotation)

[0020] Preferably, no minerals such as iron or copper are added, as they are catalysts for fat oxidation. Oxygen absorbers, such as sodium ascorbate, can also be added to the cereal based food product comprising DHA.

[0021] The cereal based food product according to the invention can have different shapes or appearance forms. For example, it can be shaped as a stick, a cake, a macaroon, a bar or it can be in form of muesli (free cereals) or flakes. It can be consumed alone or in association with dairy products such as milk, yogurts, cottage cheeses, or the like. A preferred product appearance is a cereal bar of 23 grams.

[0022] Another aspect of the present invention relates to a packaged food product comprising a package including, under modified atmosphere, the cereal based food product described above. Preferably, the cereal based food product is shaped as a bar and the modified atmosphere contains less than 0.5 vol-% of molecular oxygen.

[0023] If the cereal based food product according to the invention has to be stored for more than a week, before being consumed, which is generally the case, it is essential to do it under modified atmosphere. The product can be packed by sealing the pouches in a glove compartment filled with inert gas. The inert gas can be any gas known by the skilled person for its use in food-containing packaging, such as N_2, CO_2 and mixtures thereof.

[0024] The longer the cereal based food product is stored, the more important is that this takes place under modified atmosphere. Indeed, if said food product is stored less than one week before its consumption, a modified atmosphere, although preferable, is not necessary.

[0025] Intermediate storage of DHA bars is also preferably done under a modified atmosphere, for example in an Atlas Lyophilisator under N_2. The primary packaging of the bars can be processed in two steps: during the first step, the bars are packed individually in an oxygen-tight pouch, and during the second step the bars are packed under protection of inert gas (for example N_2) by sealing the pouches in a glove compartment filled with N_2.

[0026] According to another aspect of the invention, there is a process for making a cereal based food product, particularly shaped as a bar, comprising DHA with no off-taste and odor, even at high concentrations of DHA. Accordingly, DHA is encapsulated by any food grade encapsulation process known by the skilled person. The encapsulation must lead up to an embedded encapsulation wherein exchanges with the other components of the bar and the atmosphere are as reduced as possible. Then, DHA is mixed with cereals such as, for example, corn flakes, rice crisps, shredded wheat, oats, millet and the like, or a combination thereof. The cereals can be of any suitable form, such as flakes, crisps, and balls, among others. Citrus flavors such as orange flavors are possibly added into the cereal mix. Separately, a binder is prepared by mixing at least one sugar with an oxygen absorber, such as sodium ascorbate and,

possibly, citrus flavors. Citrus flavors are preferably added both to the cereal mix ingredients and to the binder ingredients. However, they can be added only to the cereal ingredients or only to the binder ingredients. If added both to the cereal mix and the binder, the flavors used for the cereal mix and those used for the binder are preferably the same.

[0027] The binder ingredients are pre-weighed and transferred into a cooker and mixer machine. The ingredients must be homogeneously mixed, i.e. lump-free and dissolved under stirring and target temperature and vacuum. The aim is to obtain the target water activity and then to add the DHA, sodium ascorbate and flavors at a maximum temperature of 80 °C. Preferably, the temperature throughout the whole process is comprised between 30 and 80°C, most preferably between 40 and 60°C, and in a most preferred embodiment is 50°C. This low temperature protects DHA, sodium ascorbate and flavors from oxidation and other chemical transformations.

[0028] This mix is transported to a mixer for cereal/binder blend. The binder and cereals are then homogeneously mixed and the blend is immediately used for bar forming to minimize fat oxidation, especially the oxidation of DHA.

[0029] A slab former, such as a two-roller slab former feeds the cereals and binder mass onto a belt. A compression roller assures the required height and homogeneity of the slab. A profiling roller shapes the slab into the desired shaped product stripes. After passing a cooling tunnel the product is cross cut (guillotine) and transported to the packaging area on numbered trays protected by plastic bags.

Examples

[0030] The following examples are illustrative of some of the products and methods of making the same falling within the scope of the present invention. They are not to be considered, in any way, limiting of the invention. Changes and modifications can be made with respect to the invention. That is, the skilled person will recognize many variations in these examples to cover a wide range of formulas, ingredients, processing, and mixtures to rationally adjust the naturally occurring levels of the compounds of the invention for a variety of applications.

Example 1: ingredient description of cereal bars containing DHA

[0031]

Cereals	**Functional properties**
Rice crisps	Cereal texture, taste, color
Corn flakes small	Cereal texture, taste, color
Natural Lemon flavor powder	Flavor, fish off-taste/odor masking agent
Natural Orange flavor powder	Flavor, fish off-taste/odor masking agent
Binder ingredients	
Glucose syrup	Binding, anti-crystallization agent, sweetness
Sucrose	Sweetness, filler
Fish oil concentrated powder rich in DHA	Encapsulated DHA (docosahexaenoic acid) source
Glycerol	Humectant, a_w decrease
Invert sugar syrup	Binding, anti-crystallization agent, sweetness, a_w decrease
Vegetable oil fractionated, non-hydrogenated, non-lauric	Taste, texture-lubrication
Honey	Taste, texture
Salt	Taste, a_w decrease
Sodium Ascorbate	Oxygen absorber
Honey flavor natural identical	Flavor
Natural Lemon flavor liquid	Flavor, fish off-taste/odor masking agent
Natural Orange flavor liquid	Flavor, fish off-taste/odor masking agent

Example 2: shelf life data

[0032] Shelf life tests and headspace analysis (oxidation test) were carried out at 37 °C (accelerated conditions) and at 20 °C/70 % relative humidity (rh). The products were analyzed for sensory, pentane and residual oxygen. 90 days

at 37 °C correspond to a shelf life of 12 months under ambient non-tropical conditions (about 20 °C). The bars were stored in closed tins to exclude the effect of the packaging material or in the case of the modified atmosphere packaging (MAP) in the original packs. A scale from 0-10 evaluates the taste and odor. A rating < 6 indicates a non-acceptable product.

Cereal bar DHA 300 mg/bar lemon flavored

Analysis 37 °C at days/months	start	30/1	60/2	90/3
A_w	0.37	0.36	0.37	0.37
Taste		8	8	9
Texture		ok	ok	ok
Color		good	good	good
Odor		good	good	good

Analysis 20 °C at days/months	90/3
A_w	0.37
Taste	9
Texture	ok
Color	good
Odor	good

Cereal bar DHA 300 mg/bar orange flavored

Analysis 37 °C at days/months	start	30/1	60/2	90/3
A_w	0.36	0.36	0.37	0.36
Taste		8	8	9
Texture		ok	ok	ok
Color		good	good	good
Odor		good	good	good

Analysis 20 °C at days/months	90/3
A_w	0.36
Taste	9
Texture	ok
Color	good
Odor	good

Example 3: shelf life data of DHA bars without the combination of Citrus flavors and MAP

[0033] Series of cereal based food products with DHA 200, 300, 400 mg/bar were produced without citrus flavor and without MAP. All products showed already after 1 month shelf life at 37°C a strong fish off-taste and odor, while the water activity, moisture, pentane and residual oxygen were comparable to the reference product.

[0034] A triangular test was carried out with a DHA bar 200 mg/bar (without citrus flavored and without MAP) against a reference bar. The samples were fresh, i.e. only one week aged.

[0035] The triangular test was significant in the sense that 16 out of 21 found a difference (99% level). However, 10 out of the 16 found attributes like fruity, honey - positive attributes, and only 6 out of the 16 found a negative off-taste like metallic, rancid. Overall, only one person identified a fish off-taste in the fresh bars, i.e. only one week aged.

Cereal bar 300 mg/bar lemon flavored without MAP

Analysis 37 °C at days/months	start	30/1	60/2	90/3
A_w		0.28	0.28	0.28
Moisture %	5.15			
Taste		7*	out**	
Texture		good		
Color		good		
Odor		good	out**	
Pentane, ppm		0.04	0.07	0.45
Residual oxygen, %		20.7	20.6	21

Analysis 20 °C at days/months	90/3
A_w	0.29
Taste	6*
Texture	good
Color	good
Odor	slight-off*
Pentane, ppm	0.02
Residual oxygen, %	20.6

Cereal bar DHA 200 mg/bar without citrus flavors but with MAP

Analysis 37 °C at days/months	start	30/1	60/2	90/3	120/4
A_w		0.26	0.27	0.27	0.28
Moisture %	5.09				
Taste		9	7*	6*	out**
Texture		good	ok	good	
Color		good	good	good	
Odor		good	good	good	out**

Analysis 20 °C at days/months	90/3
A_w	0.26
Taste	6*
Texture	good
Color	good
Odor	good

Cereal bar DHA 400 mg/bar without citrus flavors but with MAP

Analysis 37 °C at days/months	start	30/1	60/2	90/3	120/4
A_w		0.28	0.30	0.28	0.29
Moisture %	5.19				
Taste		8*		6*	out**
Texture		good		ok	ok
Color		good		good	ok
Odor		good		good	out**

Analysis 20 °C at days/months	90/3
A_w	0.28
Taste	6*
Texture	ok
Color	good
Odor	good

In the previous tables of this example, the sign * means slight fish-off taste and odor, and the sign ** means strong fish-off taste and odor

Claims

1. Cereal based food product having a water activity between 0.2 and 0.4 and comprising encapsulated DHA and one or more citrus flavors.

2. Cereal based food product according to claim 1 wherein the effective amount of DHA does not exceed 2200 mg per 100 g food product.

3. Cereal based food product according to claim 2 wherein the effective amount of DHA does not exceed 1800 mg per 100 g food product.

4. Cereal based food product according to claim 2 wherein the effective amount of DHA is 1300 mg per 100 g food product.

5. Cereal based food product according to one of claims 1 to 4 wherein the one or more citrus flavors are present in an amount varying between 0.01 and 0.20 wt-%.

6. Cereal based food product according to claim 5 wherein the one or more citrus flavors are present in an amount varying between 0.10 and 0.15 wt-%.

7. Cereal based food product according to claim 5 wherein the on or more citrus flavors are present in an amount of 0.13 wt-%.

8. Cereal based food product according to one of claims 1 to 7 wherein the one or more citrus flavors are chosen among the group consisting of orange flavor, lemon flavor, grapefruit flavor and mixtures thereof

9. Cereal based food product according to one of claims 1 to 8 having a water activity between 0.28 and 0.38.

10. Cereal based food product according to claim 9 having a water activity of 0.33.

11. Cereal based food product according to any preceding claim further comprising at least one of glycerol, honey, prebiotics, probiotics, antioxidants and oxygen absorbers.

12. Cereal based food product according to any preceding claim wherein the food product is shaped as a stick, a cake, a macaroon, a bar or is in form of muesli or flakes.

13. Cereal based food product according to claim 12 wherein the food product is shaped as a bar.

14. Packaged food product comprising a package including a cereal based food product according to one of claims 1 to 13 under modified atmosphere.

15. Packaged food according to claim 14 wherein the modified atmosphere contains less than 0.5 vol-% of molecular oxygen.

16. Packaged food according to claim 14 or 15 wherein the cereal based food is shaped as a bar.

17. Process for making a cereal food product according to one of claims 1 to 13 comprising the steps of

(1) preparing a cereal mix by mixing cereals, encapsulated DHA and possibly one or more citrus flavors,
(2) preparing a binder possibly containing one or more citrus flavors,
(3) mixing the product obtained under (1) and the product obtained under (2) to obtain the cereal food product,

wherein at least one of the products obtained under (1) and (2) includes one or more citrus flavors and the temperature throughout the whole process does not exceed 80°C.

18. Process according to claim 17 wherein the temperature throughout the whole process does not exceed 50°C.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 02 01 7803

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	30 January 2003	Vuillamy, V

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X : particularly relevant if taken alone
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A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 02 01 7803

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
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CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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& : member of the same patent family, corresponding document

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 02 01 7803

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

19 REPUBLIC OF FRANCE

11 Publication No.: 2,758,055

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51 Int. Cl.[6]: A 23 L 1/325, A 23 L 1/29, A 23 D 9/05

12 APPLICATION FOR PATENT OF INVENTION A1

22 Filing date: 01/06/97

30 Priority

43 Date of public access to the application: 07/10/98 Bulletin 98/28

56 List of documents cited in the preliminary search report: *See end of this document*

60 Reference to other related French documents:\

71 Applicant(s): SEAL OIL – FR

72 Inventor(s): BARRIER, PASCALE and ROUSSEAU, JEAN YVES

73 Assignee(s):

74 Agent: CABINET HERRBURGER

54 MICROENCAPSULATED POWDER BASED ON FISH OIL RICH IN POLYUNSATURATED FATTY ACIDS

57 Microencapsulated powder that is dispersible in water, even cold water, being highly flowable, based on fish oil rich in polyunsaturated fatty acids fixed on a solid matrix and obtained by low-temperature emulsion and drying in an atomization tower, characterized in that it includes at least 25% and preferably about 30% by weight of oil fixed on a matrix based on a colloidal substance associated with one or more carbohydrates.

This invention concerns a powder made of microcapsules that are dispersible in water, even cold water, presenting good flowability, based on fish oil that is rich in polyunsaturated fatty acids fixed on a solid matrix and obtained by a process of emulsion and drying at low temperature in an atomization tower.

It is well known, and has been known for a number of years, that oils extracted from fatty fish have particular health benefits because of their high polyunsaturated fatty acid content.

For this reason, manufacturers are currently marketing nutritional supplements based on oil from fatty fish; this oil is available in raw form, refined form, or as oil that has undergone molecular changes by chemical or enzymatic treatment to obtain enhanced concentrations of polyunsaturated fatty acids.

These preparations, which are extracted particularly from mackerel, herring, pollock, sardines, or tuna, are usually in liquid form, and present the disadvantage of being highly sensitive to oxidation, particularly under the effect of light or oxygen from the air, which alters the double bonds of the polyunsaturated fatty acids and therefore results in loss of the beneficial properties of these oils.

To address this problem and to increase the shelf life of these oils, it has been suggested that they undergo treatment permitting them to be packaged in the form of microencapsulated powder.

This treatment, which is a known type, consists essentially of adding a solution of absorbing agents to the oil to be treated, then homogenizing the resulting mixture to emulsify the oil as fine droplets in this solution before the homogenized mixture is sent to an atomization tower to evaporate the water and produce microcapsules formed from the oil droplets fixed on a matrix of the absorbing agents.

However, these known powders are distinguished by a relatively low content of fish oil, insufficient flowability, and limited compressibility, which prevents them from being presented in tablet form.

In addition, these powders are not immediately water-dispersible, and they can be dispersed only under special conditions of temperature and pressure.

The aim of this invention is to address these problems by offering a powder of the above-mentioned type, particularly one that is distinguished by good flowability and that disperses readily in water, even cold water (from the tap) at normal pressure, providing an emulsion that is homogeneous and stable over time.

In accordance with the invention, this powder is characterized in that it contains at least 25%, preferably about 30% by weight of an oil fixed on a matrix based on a colloidal substances associated with one or more carbohydrates.

It has been found that such a powder can, without losing its intrinsic qualities, be stored for a long time under nitrogen and in a cool, dark location.

This substance is preferably associated with maltodextrin or cyclodextrin.

More specifically, and according to another characteristic of the invention, the matrix contains 70 to 85% colloidal substances, particularly modified starch, and between 15 and 30% maltodextrin or cyclodextrin.

To improve the resistance of the above-mentioned power to oxidation and light, it has been suggested in accordance with a preferred characteristic of the invention, that the microcapsules of this invention be coated with a coating agent that acts as a protective barrier to prevent the development of oxidation factors.

Complementary coating of this kind can be accomplished by injecting the coating agent on a fluidized bed directly into the atomization tower, or mixing it with the initial emulsion.

Various tests have established that the coating agent may advantageously be gum arabic.

In one particularly advantageous embodiment, the powder according to the invention has the following composition by weight:

-fish oil: 27 to 32%, advantageously 30%

-modified starch: 45 to 55%, advantageously 51%

-maltodextrin or cyclodextrin: 10 to 20%, advantageously 15%

-gum arabic: 2 to 6%, advantageously 4%

In another characteristic of the invention, the powder presents a substantially homogeneous particle size averaging 300 μm.

It should be noted that such a substantially homogeneous particle size can be obtained by recycling and agglomeration of the dust or "fines" in the atomization tower.

A powder according to the invention based on herring oil and having a moisture content of 5.96% presents, as an example, the particle size shown in the table below:

Size (μm)	Fraction (%)	Cumulative (%)
500	13.1	13.1
300	51.1	64.2
200	25.5	89.7
100	1.03	100
<100	0	100

The mean particle size D50 of this powder is 314 μm.

The attached figure represented the particle size range of this powder.

In this figure, the x-axes represent the size of the particles decreasing from left to right.

The y-axes represent percentages.

The bar chart represents the fraction in percent, and the curved line represents the cumulative percentage.

This figure clearly shows that the majority of particles in this powder are 300 μm in size.

In accordance with another characteristic of the invention, tablets can be produced by treating the above-mentioned powder with a compressibility additive, preferably colloidal silica.

It was verified that these tablets resist oxidation over time.

CLAIMS

1) Powder made of microcapsules that are dispersible in water, even cold water, having good flowability, based on fish oil that is rich in polyunsaturated fatty acids fixed on a solid matrix and obtained by a process of low-temperature emulsion and drying in an atomization tower, characterized in that it contains at least 25%, preferably about 30% by weight of oil fixed on a matrix based on a colloidal substance associated with one or more carbohydrates.

2) Powder according to Claim 1, characterized in that the matrix contains modified starch.

3) Powder according to either of Claims 1 and 2, characterized in that the matrix contains maltodextrin or cyclodextrin.

4) Powder according to Claim 3, characterized in that the matrix contains 70 to 85% colloidal substance, particularly modified starch, and 15 to 30% maltodextrin or cyclodextrin.

5) Powder according to any of Claims 1 to 4, characterized in that it is made up of microcapsules coated with a coating agent.

6) Powder according to Claim 5, characterized in that the coating agent is gum arabic.

7) Powder according to Claim 6, characterized in that it presents the following composition by weight:

-fish oil:	27 to 32%, advantageously 30%
-modified starch:	45 to 55%, advantageously 51%
-maltodextrin or cyclodextrin:	10 to 20%, advantageously 15%
-gum arabic:	2 to 6%, advantageously 4%.

8) Powder according to any of Claims 1 to 7, characterized in that it presents a substantially homogeneous particle size averaging 300 μm.

9) Tablets, characterized in that they are made of the powder according to any of Claims 1 to 8, treated with a compressibility additive.

10) Tablets according to Claim 9, characterized in that the compressibility additive is colloidal silica.

ILLUSTRATION
1/1

Fraction (%)
Cumulative (%)

Particle size (μm)

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PRELIMINARY SEARCH REPORT
based on the last claims filed prior to the search

2758055
National registration no:
FA 540124
FR 9700055

DOCUMENTS CONSIDERED PERTINENT

Category	Citation of the document with indication, as needed of the pertinent parts	Relevant claims of the application examined
Y	WPI DATABASE Section Ch, Week 9439 Derwent Publications, Ltd., London, GB; Class D13, AN 94-314363 XP002041987 & KR 9 310 538 B (NONG SHIM CO., LTD.) October 28, 1993 summary	1-10
Y	EP 0 180 786 A (PISTOLESI, ELVIRA) claims 1, 8; example 1	1-10
Y	FR 2 625 875 A (ASSUTECH, LTD.) claims 1, 2	1-10
Y	EP 0 462 003 A (MEDGENIX GROUP, S.A.) claims 1, 3, 7, 8	1-10
Y	EPODOC DATABASE EUROPEAN PATENT OFFICE XP002042187 & CN 1 119 070 A (BEIJING FOOD INSTITUTE) March 27, 1996 summary	1-10

TECHNICAL AREAS SEARCHED (Int. Cl. 6)

A 23 L
A 61 K

Search completion date September 30, 1997 Examiner: Caturla Vicente, V.

CATEGORY OF DOCUMENTS CITED:
X: particularly pertinent by itself
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A: pertinent with respect to at least one claim or general technological background
O: nonwritten disclosure

P: intercalary document
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E: patent document with a date prior to the filing date, not published until this filing date or a later date
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(12) DEMANDE DE BREVET D'INVENTION A1

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(56) **Liste des documents cités dans le rapport de recherche préliminaire :** *Se reporter à la fin du présent fascicule.*

(60) **Références à d'autres documents nationaux apparentés :**

(71) **Demandeur(s) :** *SEA OIL* — FR.

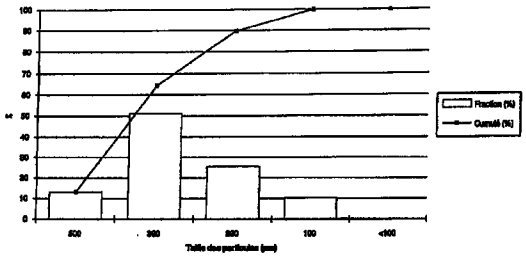
(72) **Inventeur(s) :** BARRIER PASCALE et ROUSSEAU JEAN YVES.

(73) **Titulaire(s) :** .

(74) **Mandataire :** CABINET HERRBURGER.

(54) POUDRE FORMEE DE MICROCAPSULES A BASE D'HUILE DE POISSON RICHE EN ACIDES GRAS POLYINSATURES.

(57) Poudre formée de microcapsules dispersibles dans l'eau, même froide, présentant une bonne coulabilité, à base d'huile de poisson riche en acides gras polyinsaturés fixée sur une matrice solide et obtenue par un procédé d'émulsification et de séchage à basse température dans une tour d'atomisation, caractérisée en ce qu'elle renferme au moins 25%, de préférence environ 30% en poids d'huile fixée sur une matrice à base d'une substance colloïdale associée à un ou plusieurs glucides.§.



FR 2 758 055 - A1

La présente invention concerne une poudre formée de microcapsules dispersibles dans l'eau, même froide, présentant une bonne coulabilité, à base d'huile de poisson riche en acides gras polyinsaturés fixée sur une matrice solide et obtenue par un procédé d'émulsification et de séchage à basse température dans une tour d'atomisation.

Il est bien connu, ce depuis de nombreuses années, que les huiles extraites de poissons gras présentent un intérêt tout particulier pour la santé, compte tenu de leur richesse en acides gras polyinsaturés.

Pour cette raison, les industriels proposent, actuellement sur le marché, des compléments nutritionnels à base d'huile de poissons gras, brute, raffinée ou ayant subi des modifications moléculaires par traitement chimique ou enzymatique dans le but d'obtenir des concentrations optimisées en acides gras polyinsaturés.

Ces préparations, qui sont notamment extraites de maquereaux, de harengs, de chinchards, de sardines ou encore de thons, sont, en règle générale, sous forme liquide et présentent l'inconvénient d'être très sensibles à l'oxydation en particulier sous l'effet de la lumière ou de l'oxygène de l'air, ce qui entraîne la modification des doubles liaisons des acides gras polyinsaturés, et donc la perte des propriétés bénéfiques de ces huiles.

Pour remédier à cet inconvénient et augmenter la durée de conservation de ces huiles, il a déjà été proposé de leur faire subir un traitement permettant de les conditionner sous forme de poudre formée de microcapsules.

Ce traitement, connu en lui-même, consiste schématiquement à ajouter à l'huile à traiter une solution d'agents absorbants, puis à homogénéiser le mélange ainsi obtenu, de façon à émulsifier l'huile sous forme de fines gouttelettes, dans cette solution avant d'introduire le mélange homogénéisé dans une tour d'atomisation pour permettre l'évaporation de l'eau et l'obtention de microcapsules formées par les gouttelettes d'huile fixées sur une matrice constituée par les agents absorbants.

Ces poudres connues se distinguent toutefois par une teneur relativement faible en huile de poisson, une coulabilité insuffisante et une faible aptitude à la compressibilité qui exclut toute possibilité de les présenter sous forme de comprimés.

De plus, la dispersion dans l'eau de ces poudres n'est pas immédiate et ne peut être effectuée que dans des conditions particulières de températures, voire de pression.

La présente invention a pour objet de remédier à ces inconvénients en proposant une poudre du type susmentionné, se distinguant en particulier par une bonne coulabilité et une aptitude à se disperser très facilement dans l'eau, même froide (sortie du robinet) ce dans des conditions normales de pression, en donnant une émulsion homogène et stable dans le temps.

Conformément à l'invention, cette poudre est caractérisée en ce qu'elle renferme au moins 25 %, de préférence environ 30 % en poids, d'huile fixée sur une matrice à base d'une substance colloïdale associée à un ou plusieurs glucides.

On a pu vérifier qu'une telle poudre peut, sans perte de ses qualités intrinsèques, être stockée pendant une longue durée sous azote, au frais et à l'abri de la lumière.

Conformément à l'invention, on a pu établir que la substance colloïdale peut avantageusement être constituée par de l'amidon modifié.

Cette substance est préférentiellement associée à de la maltodextrine ou à de la cyclodextrine.

Plus précisément et selon une autre caractéristique de l'invention, la matrice renferme entre 70 et 85 % de substance colloïdale notamment d'amidon modifié et entre 15 et 30 % de malto-dextrine ou de cyclodextrine.

Pour améliorer la résistance de la poudre susmentionnée vis-à-vis de l'oxydation et de la lumière, il a été proposé, conformément à une caractéristique préférentielle de l'invention, d'enrober les microcapsules constitutives de celle-ci dans un agent enrobant faisant office de barrière de protection de nature à prévenir le développement des facteurs d'oxydation.

Un tel enrobage complémentaire peut être effectué en injectant l'agent enrobant sur lit fluidisé directement dans la tour d'atomisation ou en le mélangeant à l'émulsion initiale.

Différents essais ont permis d'établir que l'agent enrobant peut, avantageusement, être constitué par de la gomme arabique.

Conformément à un exemple de réalisation particulièrement avantageux, la poudre selon l'invention présente la composition pondérale suivante :

- huile de poisson : entre 27 et 32 % et notamment 30 %
- amidon modifié : entre 45 et 55 % et notamment 51 %
- malto-dextrine ou cyclodextrine : entre 10 et 20 % et notamment 15 %
- gomme arabique : entre 2 et 6 % et notamment 4 %.

Selon une autre caractéristique de l'invention, la poudre présente une granulométrie substantiellement homogène centrée sur 300 μm.

Il est à noter qu'une telle granulométrie substantiellement homogène peut être obtenue grâce à un recyclage et une agglomération des poussières ou « fines » dans la tour d'atomisation.

Une poudre conforme à l'invention, à base d'huile de harengs et ayant un taux d'humidité de 5,96 % présente, à titre d'exemple, la granulométrie mentionnée dans le tableau ci-dessous :

Taille (μm)	Fraction (%)	Cumulé (%)
500	13,1	13,1
300	51,1	64,2
200	25,5	89,7
100	10,3	100
<100	0	100

La granulométrie moyenne d50 de cette poudre est de 314 μm.

La figure jointe en annexe représente le spectre granulométrique de cette poudre.

Sur cette figure, les abscisses représentent la taille des particules en décroissant du côté gauche vers le côté droit.

Les ordonnées représentent les pourcentages.

L'histogramme par barre représente la fraction en pourcentage et la courbe en trait plein le pourcentage cumulé.

Cette figure montre clairement que cette poudre à base d'huile de harengs présente un maximum de particules ayant une granulométrie de 300 μm.

Conformément à une autre caractéristique de l'invention, on peut obtenir des comprimés en traitant la poudre susmentionnée avec un excipient de compressibilité, de préférence de la silice colloïdale.

On a pu vérifier que de tels comprimés sont très stables dans le temps vis-à-vis des phénomènes d'oxydation.

REVENDICATIONS

1°) Poudre formée de microcapsules dispersibles dans l'eau, même froide, présentant une bonne coulabilité, à base d'huile de poisson riche en acides gras polyinsaturés fixée sur une matrice solide et obtenue par un procédé d'émulsification et de séchage à basse température dans une tour d'atomisation, caractérisée en ce qu'
elle renferme au moins 25 %, de préférence environ 30 % en poids d'huile fixée sur une matrice à base d'une substance colloïdale associée à un ou plusieurs glucides.

2°) Poudre selon la revendication 1
caractérisée en ce que
la matrice renferme de l'amidon modifié.

3°) Poudre selon l'une quelconque des revendications 1 et 2, caractérisée en ce que
la matrice renferme de la malto-dextrine ou de la cyclodextrine.

4°) Poudre selon la revendication 3,
caractérisée en ce que
la matrice renferme entre 70 et 85 % de substance colloïdale notamment d'amidon modifié et entre 15 et 30 % de maltodextrine ou de cyclodextrine.

5°) Poudre selon l'une quelconque des revendications 1 à 4, caractérisée en ce qu'
elle est constituée de microcapsules enrobées dans un agent enrobant.

6°) Poudre selon la revendication 5,
caractérisée en ce que
l'agent enrobant est de la gomme arabique.

7°) Poudre selon la revendication 6,
caractérisée en ce qu'
elle présente la composition pondérale suivante :

- huile de poisson : entre 27 et 32 % et notamment 30 %
- amidon modifié : entre 45 et 55 % et notamment 51 %
- malto-dextrine ou cyclodextrine : entre 10 et 20 % et notamment 15 %
- gomme arabique : entre 2 et 6 % et notamment 4 %.

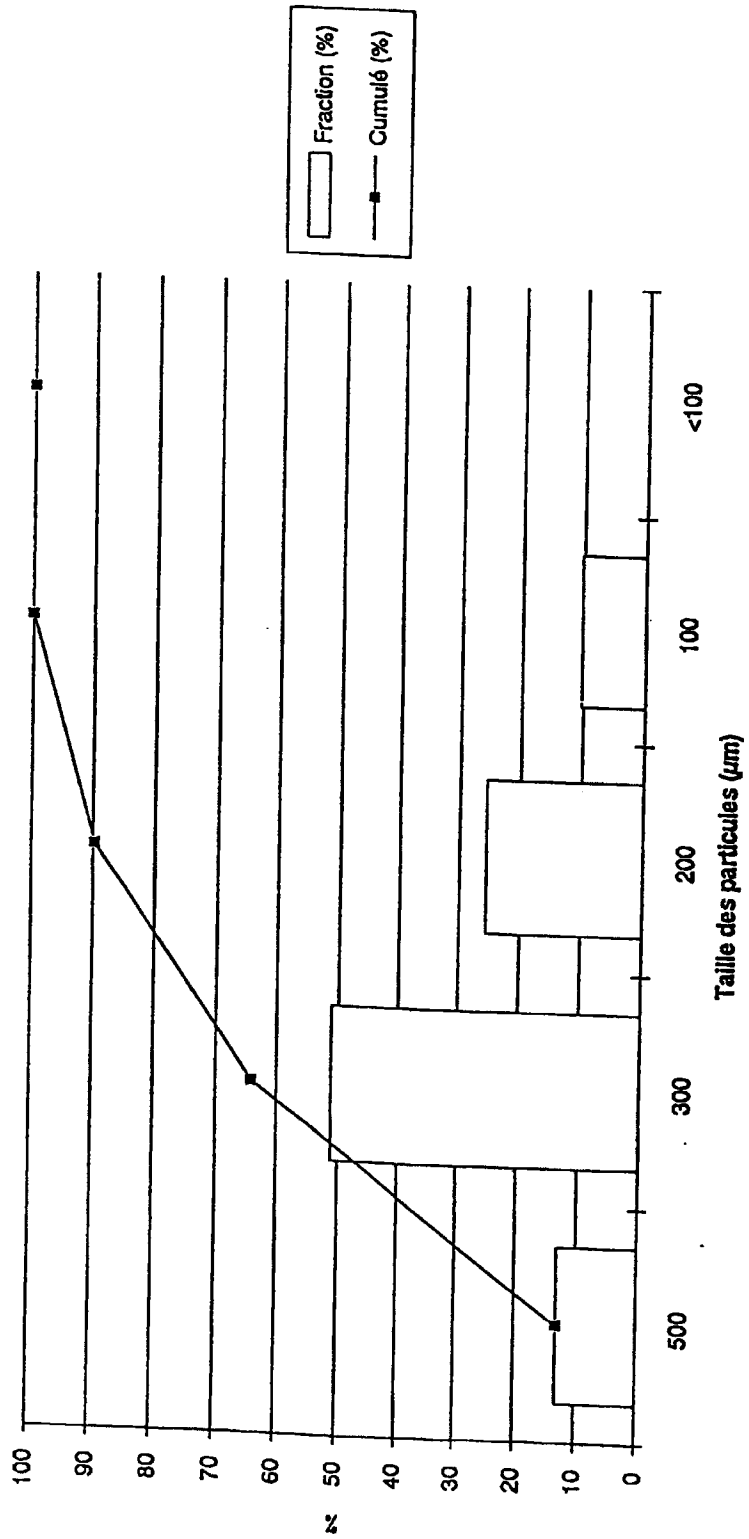
8) Poudre selon l'une quelconque des revendications 1 à 7 caractérisée en ce qu'
elle présente une granulométrie substantiellement homogène centrée à 300 μm.

9) Comprimés
caractérisés en ce qu'
ils sont constitués par de la poudre selon l'une quelconque des revendications 1 à 8, traitée avec un excipient de compressibilité.

10°) Comprimés selon la revendication 9,
caractérisés en ce que
l'excipient de compressibilité est de la silice colloïdale.

PL UNIQUE

1/1


Fraction (%)
Cumulé (%)
100
90
80
70
60
50
40
30
20
10
0
%
<100
100
200
300
500
Taille des particules (µm)

2758055

REPUBLIQUE FRANÇAISE

INSTITUT NATIONAL
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PROPRIETE INDUSTRIELLE

RAPPORT DE RECHERCHE PRELIMINAIRE

établi sur la base des dernières revendications déposées avant le commencement de la recherche

N° d'enregistrement national

FA 540124
FR 9700055

DOCUMENTS CONSIDERES COMME PERTINENTS		Revendications concernées de la demande examinée
Catégorie	Citation du document avec indication, en cas de besoin, des parties pertinentes	
Y	DATABASE WPI Section Ch, Week 9439 Derwent Publications Ltd., London, GB; Class D13, AN 94-314363 XP002041987 & KR 9 310 538 B (NONG SHIM CO LTD) , 28 octobre 1993 * abrégé * ---	1-10
Y	EP 0 180 786 A (PISTOLESI, ELVIRA) * revendications 1,8; exemple 1 * ---	1-10
Y	FR 2 625 875 A (ASSUTECH LTD) * revendications 1,2 * ---	1-10
Y	EP 0 462 003 A (MEDGENIX GROUP SA) * revendications 1,3,7,8 * ---	1-10
Y	DATABASE EPODOC OFFICE EUROPÉEN DES BREVETS XP002042187 & CN 1 119 070 A (BEIJING FOOD INST) 27 mars 1996 * abrégé * -----	1-10

DOMAINES TECHNIQUES RECHERCHES (Int.Cl.6)
A23L A61K

Date d'achèvement de la recherche	Examinateur
30 septembre 1997	Caturla Vicente, V

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O : divulgation non-écrite
P : document intercalaire

T : théorie ou principe à la base de l'invention
E : document de brevet bénéficiant d'une date antérieure à la date de dépôt et qui n'a été publié qu'à cette date de dépôt ou qu'à une date postérieure.
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